MLE 5003 Final Report

Upcycling Waste Plastics into Value-added Products

(Research on the Upcycling of PEG)

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1. Introduction

Plastics have become an indispensable material in modern life, with their low cost, durability, and chemical diversity driving widespread use across agriculture, electronics, construction, packaging, and other sectors. However, this reliance also poses severe challenges: in 2019, 368 million tons of plastic were produced globally, with most ending up in landfills or the natural environment. The pandemic further exacerbated polymer production due to a surge in demand for disposable masks and packaging, highlighting the growing issue of microplastic pollution[1]. It is estimated that the full lifecycle of plastics incurs a direct economic loss of $80 billion annually. If current trends continue, plastic carbon emissions are projected to reach 6.5 billion tons of CO_2e by 2050, accounting for 15% of the global carbon budget. Notably, recycling plastics globally could save an amount of energy equivalent to 3.5 billion barrels of oil each year.

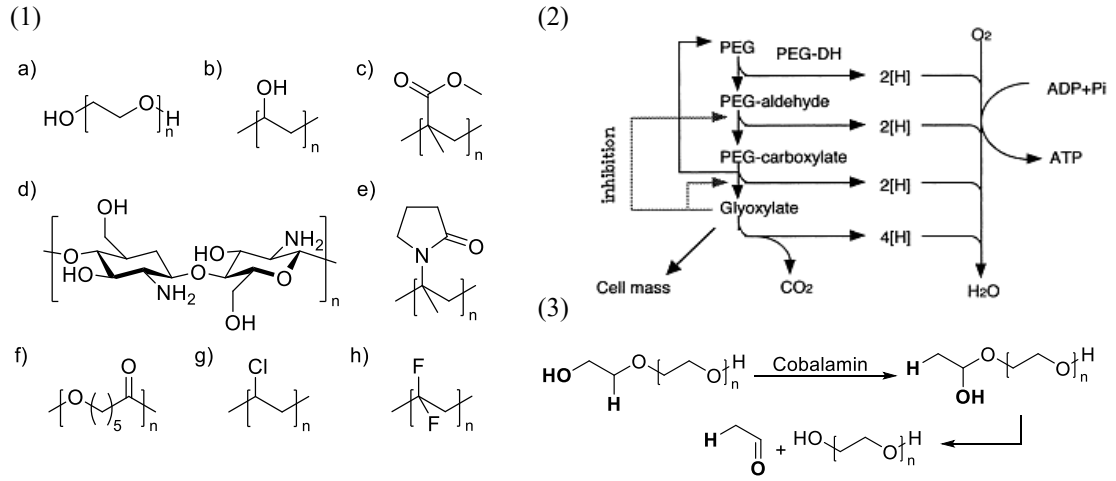


Figure 1 (1) Chemical structures of some polar polymers widely used for polyelectrolytes: (a) Polyethylene oxide, (b) Polyvinyl alcohol, (c) Polymethyl methacrylate, (d) Chitosan, (e) Polyvinylpyrrolidone, (f) Poly(3-caprolactone), (g) Polyvinyl chloride, and (h) Polyvinylidene fluoride.[2] (2) Aerobic metabolic pathway for PEG. (3) Anaerobic metabolism of PEG[3]

Simultaneously, the energy sector is rapidly advancing clean technologies such as fuel cells and solar cells to replace fossil fuels. In this transformation, functional polymers, such as polyelectrolytes used as solid-state battery electrolytes, are widely employed but bring accompanying waste management challenges. For example, although polyethylene glycol (PEG) offers excellent ionic conductivity, the degradation challenges following its large-scale use remain unresolved. Therefore, developing green degradation technologies

for plastics and functional polymers to build a "production-application-recycling" sustainable cycle has become essential for achieving environmental and economic wins. This breakthrough is crucial not only for pollution control but also for global energy restructuring and carbon emission reduction goals.

Current plastic recycling technologies fall into four main categories, each with distinct characteristics and applicable scenarios. Traditional incineration and landfill methods are being phased out due to high pollution and low economic returns. Mechanical recycling, while suitable for large-scale applications and lower in CO_2 emissions, faces issues such as reduced performance and color residue in recycled plastics. In contrast, chemical recycling technologies show greater potential. Electrocatalytic methods, utilizing renewable electricity under mild conditions for efficient transformation of plastics, have made significant breakthroughs; enzymatic catalysis offers specific degradation via biocatalysts, showing unique advantages under mild conditions[4-17].

Taking PEG as an example, the choice of degradation pathways must consider molecular weight and environmental factors. Low-molecular-weight PEG (400-4000 Da) can be biodegraded by various microorganisms under aerobic conditions through the action of oxidases and dehydrogenases, ultimately producing small molecules such as ethylene glycol; in anaerobic environments, specific enzyme systems rely on molecular rearrangement mechanisms. For higher-molecular-weight PEG (6000-20000 Da), biodegradation efficiency significantly decreases, where non-biological methods demonstrate unique advantages. By precisely controlling temperature, pH, and other parameters, non-biological degradation can overcome molecular weight limitations and selectively produce high-value products, which is challenging for biological methods.

This logical approach to technology selection is also applicable to the recycling of other plastics. In practice, the most suitable degradation strategy must be chosen based on the type of plastic, molecular characteristics, and expected products. Future development will focus on optimizing combinations of different technologies, such as integrating biological pretreatment with chemical catalysis or developing new photo-electrocatalytic systems, to achieve more efficient and economical plastic recycling.

2. General Mechanism of Polymer Oxidative Degradation

Oxidative degradation of polymers starts with the generation of free radicals on the main chain, typically requiring high energy sources like ultraviolet light or high temperatures to break polymer bonds or from radical initiators like peroxides. These radicals react with oxygen to form unstable peroxy radicals, which can follow two main degradation pathways. In pathway A, peroxy radicals abstract hydrogen atoms from C-H bonds, forming peroxide groups and oxygen-centered radicals when the O-O bonds cleave[18]. Pathway B, a Russell-type mechanism, involves the coupling of two peroxy radicals to eventually produce two oxygen-centered radicals, which can lead to the formation of ketones and alcohols through β-scission or hydrogen atom transfer[19].

Despite the detailed understanding of these mechanisms, the natural autoxidation rate of plastics is slow and often incomplete due to their chemical inertness, leading to a low concentration of polymer radicals under mild conditions. To enhance the degradation rate, researchers employ external stimuli such as heat and light in laboratory settings, using high temperatures (>200 °C) or intense ultraviolet light (254 nm) to increase reactive oxygen species (ROS) levels[20,21]. However, the harsh conditions required limit the industrial application of these strategies due to high energy costs and safety concerns.

3. Recent Advances in Thermocatalytic Oxidative Degradation

3.1 Thermal Oxidative Degradation of Polymers Using Molecular Oxygen Alone

The thermal oxidative degradation of polymers has been extensively studied in both natural environments and laboratory settings because heat is easily applied to chemical reactions. There are numerous examples in the literature, such as reference 46, of thermal oxidative degradation without external chemical reagents. When these polymers are exposed to high temperatures in the presence of air, they undergo oxidative chain scission and transform into small molecular oxidized products[18,22]. However, this method has three distinct disadvantages. First, the technique is inefficient at mild temperatures, such as room temperature, thus oxidative degradation must be conducted under harsh conditions requiring more energy. Considering the disposal of millions of tons of waste plastics, constructing a large reactor that demands high maintenance and operational costs is

economically unfeasible. Second, the risk of explosion increases with temperature in the presence of oxygen, making safety another major concern. Lastly, the formation of unwanted by-products is more likely at extreme temperatures. Due to many C-C bond-breaking events leading to an uncontrollably high concentration of free radicals, these radicals are prone to engage in side reactions such as radical-radical coupling, elimination, and hydrogen atom transfer (HAT), rather than being captured by molecular oxygen[23]. Therefore, to address these issues, lowering the temperature while simultaneously accelerating the efficiency of oxidative degradation would be more advantageous.

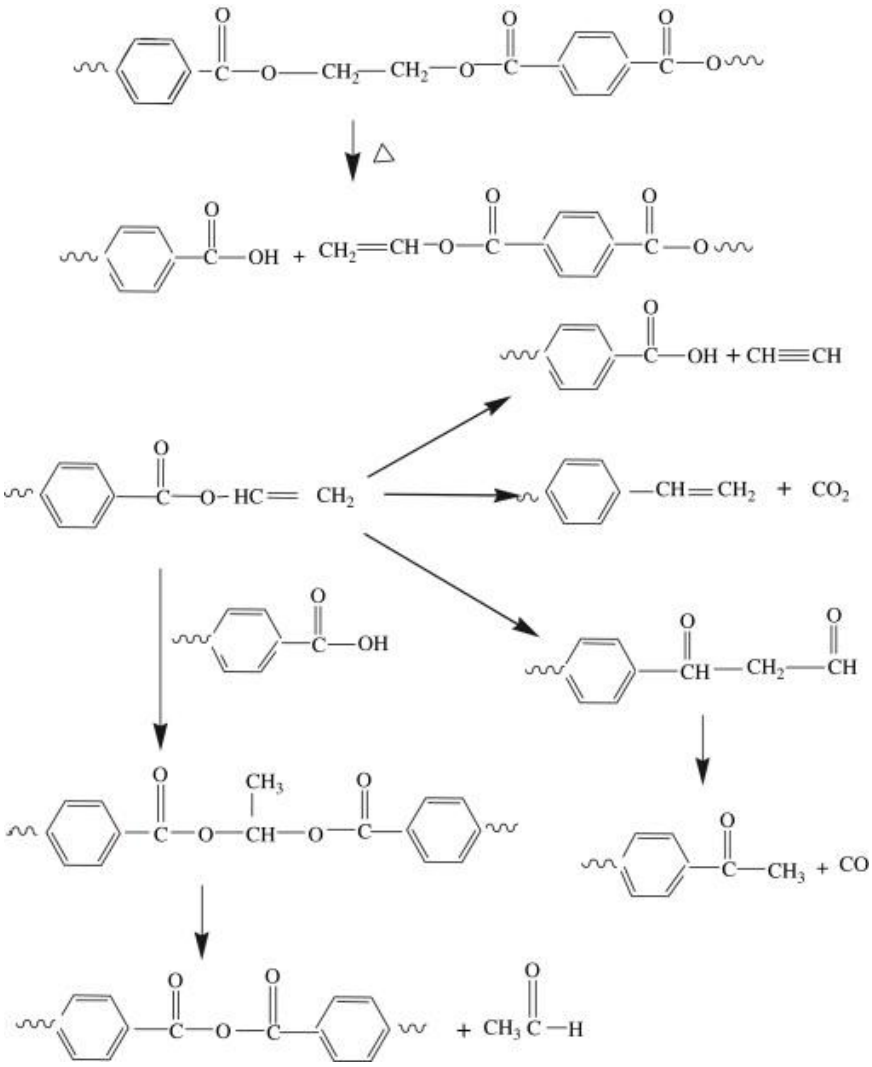
3.2 Thermocatalytic Oxidative Degradation of Polymers

Under normal conditions, photochemical degradation and thermal degradation are similar and classified as oxidative degradation. The main difference between the two lies in the sequence of the initial steps leading to the autoxidation cycle. Other differences include that thermal reactions occur throughout the bulk of the polymer sample, while photochemical reactions only occur on the surface. Thermal degradation of polymers is induced by thermolysis and ultraviolet light, leading to random and chain scission (depolymerization). Depolymerization reactions in thermal degradation do not need to be initiated at the ends of the macromolecules; instead, defects in the chain structure (such as initiator fragments or peroxide or ether linkages) form weak links where depolymerization starts. A significant amount of addition polymers depolymerize at high temperatures, for example, polymethyl methacrylate (PMMA) is almost quantitatively converted to monomer, while PE has already decomposed into longer olefin segments, actually producing very little monomer. Thermal degradation above 200 °C leads to chain scission, which largely depends on impurities such as unsaturated sites, head-to-head units, etc. Polyolefins are well-known to be sensitive to thermal oxidation, as impurities are produced at high temperatures during their manufacturing process. Drago et al. studied the thermally stimulated oxidative degradation of high-impact PS by nitric acid. The mechanisms of oxidation and nitration depend on the temperature, leading to molecular and chemical heterogeneity in the polymers, and reducing their mechanical properties. PS thermally degrades into organic compounds such as phenol, quinone, naphthalene, and diphenylamine at experimental temperatures of 350-450 °C[24]. The

complex reactions occurring during polymer thermal degradation depend on various factors such as heating rate, pressure, reaction medium, and reactor geometry. Polymers have high viscosity, which hinders heat and mass transfer, complicating the process. The thermal oxidative degradation of polyesters produces a variety of products such as formaldehyde, acetaldehyde, formic acid, acetic acid, CO_2, and H_2O. In addition to these compounds, small amounts of various other compounds such as hydroxy aldehydes, hydroxy acids, and aldonic acids were also found.

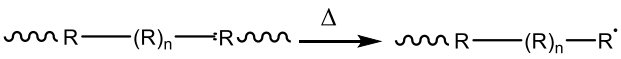
Mechanism of Thermal Degradation

The thermal degradation of polymers involves complex reactions crucial for understanding their processing and recycling, typically following two main pathways: chain-end degradation and random scission. Chain-end degradation, also known as depolymerization, initiates at the polymer chain ends and sequentially releases monomer units, effectively reversing the propagation step in addition polymerization via a free radical mechanism. For instance, poly(α-methylstyrene) synthesized through an anionic process can completely revert to monomer when heated[25]. This type of degradation gradually reduces the molecular weight while releasing monomers, primarily occurring in polymers like PMMA, poly(α-methylstyrene), and polytetrafluoroethylene where the main chain bonds are weaker than the side group bonds and the polymer chains possess active ends such as radicals or ions. Random scission can occur at any point along the polymer chain, leading to lower molecular weight fragments rather than monomers and doesn't require the presence of active sites on the polymer chain[25]. Vinyl polymers like polystyrene and polyacrylonitrile typically undergo this process, resulting in low monomer yields with the degradation products being larger than the monomers themselves. For example, poly(ethylene terephthalate) degrades via random thermal routes (Scheme 1), beginning with carboxyl and vinyl group fractures[26]. In general, initiation reaction occurs by random chain scission or chain end initiation. This step is followed by de-propagation step forming monomer. Termination takes place through radical coupling and radical disproportionation (Scheme2).

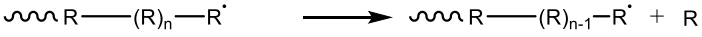


Scheme 1.

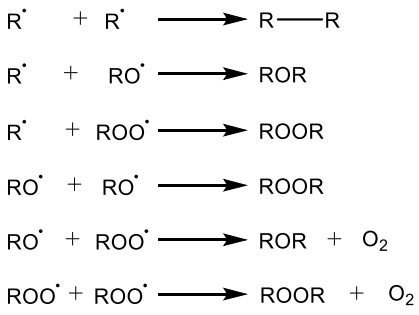
Initiation



Propagation



Termination



Scheme 2.

3.3. Advances in Photocatalytic Oxidative Degradation Research

The degradation and oxidation mechanisms in polymers are determined by extraneous groups and/or impurities within the polymer, which absorb light quanta and form excited states. Initially, short-lived singlet states transition into longer-lived triplet states. The excited triplet state can cleave polymer chains, forming radical pairs (Norrish Type I reaction) or through hydrogen transfer to produce saturated and unsaturated chain end pairs (Norrish Type II reaction). These polymer radicals may add molecular oxygen (in the triplet ground state) into peroxyl radicals, which extract hydrogen to form hydroperoxide groups. These groups absorb UV light or are excited by energy transfer, causing weak O-O bonds to break and form alkoxy and hydroxy radical pairs. These may react in various ways, such as hydrogen abstraction, chain scission, rearrangement, etc., accelerating photodegradation. Double bonds may add singlet excited oxygen molecules. In this reaction, the double bond transfers to adjacent C-C bonds, forming hydroperoxide groups. Some synthetic polymers, like aromatic polyesters and polyamides, possess inherent UV absorption capabilities, leading to excitation, radical formation, oxygenation, small molecule cleavage, and chain breaking. Some of these polymers automatically stabilize against photodegradation by forming oxidized surface layers that highly absorb near-UV and short-wavelength visible light, preventing further penetration of light into deeper layers.

4. The main focus of this study

Generally, PEG biodegradation could be roughly divided into two pathways, which are aerobic and anaerobic. In aerobic environments, enzymatic reactions involving oxidases and dehydrogenases oxidize PEG molecules into aldehydes and carboxylic acids, followed by ether bond cleavage, which reduces the molecular length. This process would also generate smaller metabolic byproducts, such as ethylene glycol and glyoxylic acid. In anaerobic conditions, PEG degradation would perform through an alternative intramolecular rearrangement mechanism, primarily relying on acetaldehyde-cleaving enzymes and glycol dehydratases to produce acetaldehyde. Also, in the study of PEG biodegradation, polymer molecular weight significantly influences its biodegradability.

Lower molecular weight PEGs (e.g., PEG 400–4000) are readily assimilated by various bacterial species, which could utilize PEG as their sole carbon and energy source[27]. In contrast, the degradation of high molecular weight PEGs (e.g., PEG 6000–20,000) relies on a limited number of bacterial species[28,29]. While PEG with molecular weights up to 20,000 Da, could only be biodegraded under certain condition[30]. Overall, both aerobic or anaerobic PEG biodegradation would be significantly affected by molecular weight, environmental conditions, microbial species, and auxiliary agents. Particularly in aquatic ecosystems, in which the metabolism primarily depends on biological oxidation mechanisms, portions of PEG may be broken down into carbon dioxide and water, which leading to a reduced yield of final products.

Compared to biological approaches, non-biological methods are easier to control and offer greater flexibility in reaction conditions, allowing for high or low temperatures and the use of strong acids or bases without needing to maintain a bio-compatible environment. By manipulating experimental conditions in non-biological methods, it is potentially to achieve higher selectivity value-added products, which were rarely found via biological pathways. In this report, we observed that the effect of cobalt acetate in the non-biological degradation of PEG-2000 with the presence of hydrogen peroxide under aqueous conditions. Furthermore, we discussed several factors that could affect the production of polyethylene glycol formate ester.

2. Experimental Preparation

(1) Materials and characteristics

All reagents were purchased from commercial sources and used without further purification unless stated otherwise. Cobalt (II) acetate (>99%), Iron(III) chloride, Manganese(II) acetate(>98%), Copper(II) sulfate, Vanadium(IV) oxide sulfate hydrate, Gadolinium(III) acetate hydrate (>99.90%), Silver acetate, Copper(II) acetate(>98%),

Sodium acetate anhydrous, Cobalt(II) nitrate hexahydrate(>98%), H_2O_2 (35% w/w aq.)TBHP (70% w/w aq.), m-CPBA, benzoate peroxide, polyethylene glycol (PEG-600; PEG-20000; PEG-4000; PEG-6000; PEG-20000), Nitric acid, Acetic Acid (>99.5%), Formic Acid (>95%), Hydrochloric acid (>37%), Diethylene glycol, Titanium (IV) isopropoxide were purchased from Sigma-Aldrich. Trifluoromethanesulfonic acid(>98%) was purchased from TCI. Ethylene Glycol was purchased from JT Baker. DI water (18.1 MΩ·cm) was used throughout the work. ^{1}H nuclear magnetic resonance (NMR) was recorded using a JEOL 400 MHz spectrometer (Tokyo, Japan) in $CDCl_3$. The chemical shift was recorded in ppm. MS spectrum was recorded using LC-MS (Shimadzu LCMS 9030)

(2) General procedures of oxidative degradation

To a 4 mL vial with a rubber cap, was weighed 100 mg PEG-2000 (2.3 mmol to repeating units), 6.0 mg $Co(OAc)_2 \cdot 4H_2O$ (2.3 μmol, 1.0 mol %), and 2.0 mL DI water. The mixture was stirred for 0.5 min to form a clear solution, followed by adding 230 μL H_2O_2 (35% w/w, 2.3 mmol, 1.0 equiv.) via syringe. Then the reaction was stirred for 22 hours under 40 °C oil bath. After desired reaction time, the reaction mixture was extracted by chloroform and diluted for NMR test directly without further purification.

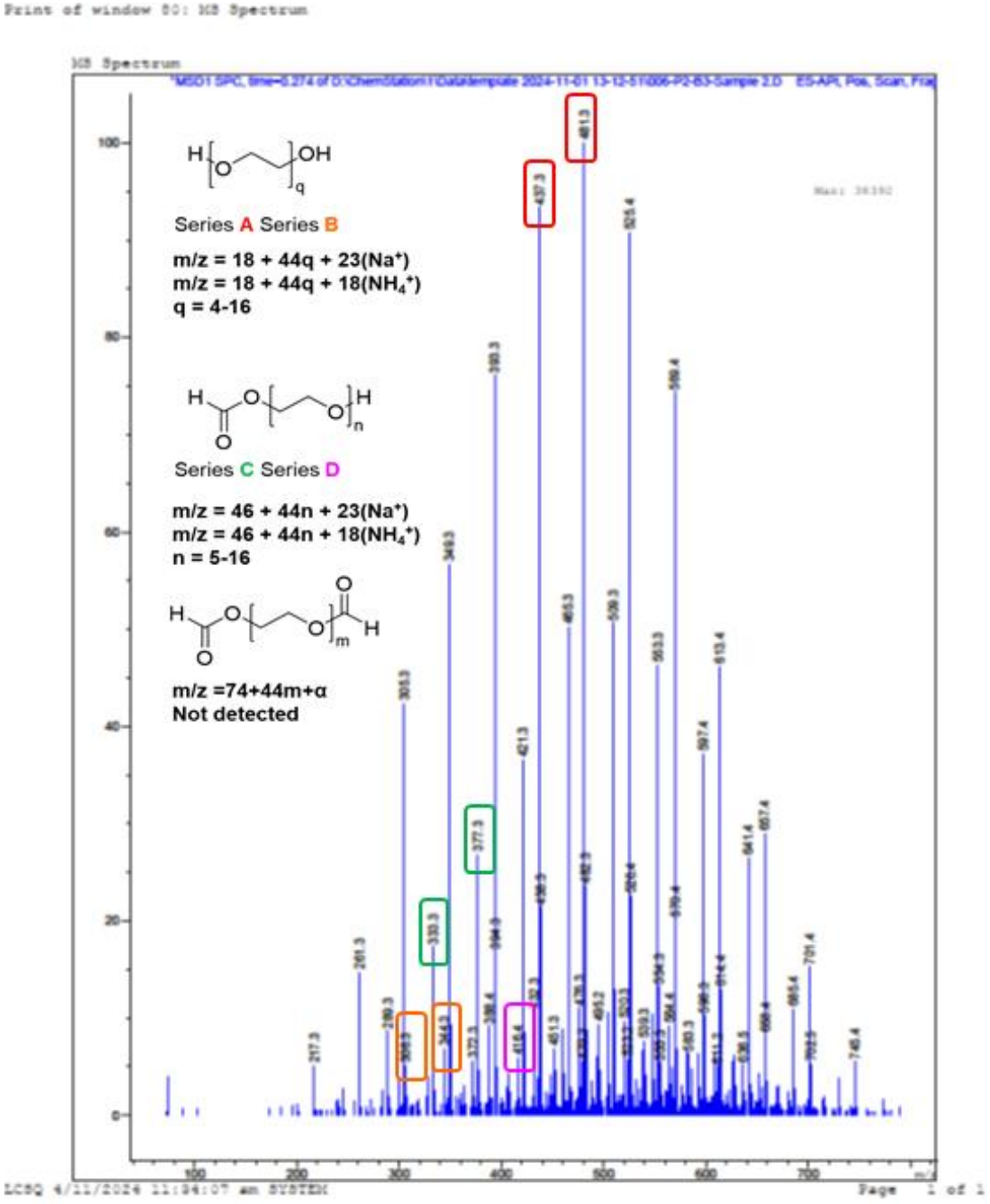
(3) Calculation Method

To further evaluate the efficiency of polyethylene glycol (PEG) conversion during oxidative degradation, quantitative analysis of the reaction products was performed using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. By integrating characteristic proton signals, the proportion of ethylene glycol (EG) units that underwent oxidation relative to the total EG units can be determined, providing a measure of the **degree of oxidation**. This metric reflects both the catalytic activity and selectivity of the system and offers a quantitative basis for comparing reaction efficiencies under different conditions. Accordingly, we established a calculation model based on end-group proton signals in the NMR spectrum and applied it to analyze the degradation products from each experimental group.

Determination of Oxidation Products

To calculate the degree of oxidation of PEG, it is essential to first identify the specific oxidation products formed post-oxidation. This involves determining their proportions to establish the necessary component ratios. Subsequently, this information allows us to calculate the yields of the desired oxidation products and assess the reaction's selectivity. Therefore, we performed mass spectrometry analysis on the oxidized system to precisely identify the substances present in the products.

Figure 1 Representative Mass Spectrum of PEG Oxidation


Print of window 80: MS Spectrum
MS Spectrum
Series A Series B
m/z = 18 + 44q + 23(Na+)
m/z = 18 + 44q + 18(NH4+)
q = 4-16
Series C Series D
m/z = 46 + 44n + 23(Na+)
m/z = 46 + 44n + 18(NH4+)
n = 5-16
m/z =74+44m+α
Not detected
Page 1 of 1

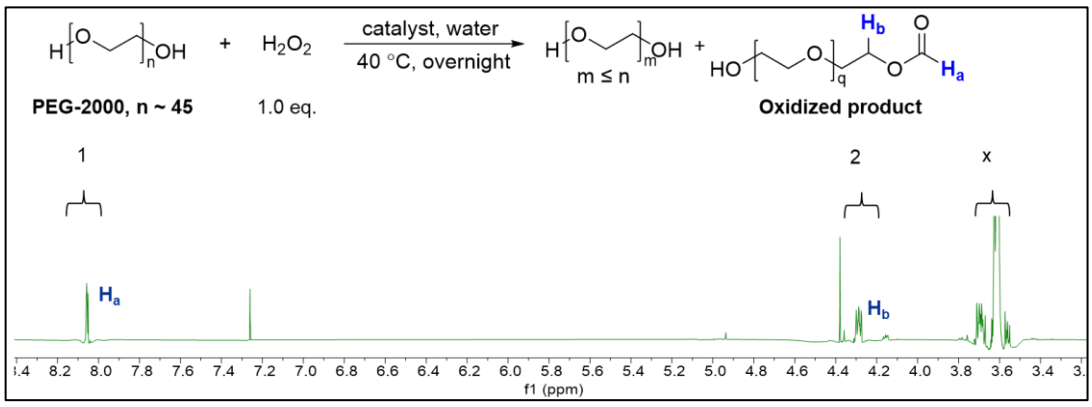
200 mg PEG, 4 mL water, 40 °C, o.n. Catalysts are metal salts with hydrate, using syringe pump to add oxidant.(flow rate: 0.9ml/10h)

All experiments underwent mass spectrometry testing, and a representative spectrum was selected for detailed analysis. From this analysis and the data obtained from the spectrum, it was determined that only formate monoesters and unreacted PEG were detected in the post-experimental products. This indicates that the reaction conditions using cobalt acetate ($Co(OAc)_2$)/hydrogen peroxide (H_2O_2) exhibit high selectivity towards the formation of formate monoesters. With this conclusion, we can now accurately calculate the extent of the oxidative reactions.

Defination of Degree of Oxidation

The oxidative degradation of polyethylene glycol (PEG-2000, n ≈ 45) was carried out using hydrogen peroxide (1.0 equiv.) as the oxidant in the presence of a cobalt-based catalyst under aqueous conditions at 40 °C overnight. The resulting products included a mixture of unreacted PEG segments and oxidized fragments containing formate end groups.

To quantify the extent of oxidation, the degree of oxidation (DO) was determined by analyzing the ^1H NMR spectrum. The signals corresponding to protons H_a (formate group, δ = 8.1 ppm), H_b (adjacent to ester, δ = 4.2 ppm), and backbone ethylene glycol protons (δ = 3.6 ppm) were used to calculate the number of reacted and unreacted ethylene glycol (EG) units.



The formula used for calculating the degree of oxidation is as follows:

$$Degree\ of\ Oxidation = \frac{\text{reacted EG units}}{\text{total EG units}} = \frac{1}{m+q+1}$$

Where:

- m, q are the numbers of unreacted EG units in the degraded and oxidized PEG chains, respectively.
- m + q is calculated from NMR integration using the formula:

$$m + q = \frac{(x + 2) - 4}{4}$$

Here, x represents the integral area of the methylene region (δ = 3.6 ppm), and the constants account for the known number of protons in reference signals.

This method provides a semi-quantitative estimation of the oxidation extent in PEG degradation via NMR analysis.

3. Experimental Procedures and Results

(1) Screening of Oxidant and Catalyst Combinations

Oxidative degradation of PEG

To a 4 mL vial with a rubber cap, was weighed 100 mg PEG-2000 (2.3 mmol to repeating units), 6.0 mg $Co(OAc)_2 \cdot 4H_2O$ (2.3 μmol, 1.0 mol %), and 2.0 mL DI water. The mixture was stirred for 0.5 min to form a clear solution, followed by adding 230 μL H_2O_2 (35% w/w, 2.3 mmol, 1.0 equiv.) via syringe. Then the reaction was stirred for 22 hours under 40 °C oil bath. After desired reaction time, the reaction mixture was extracted by chloroform and diluted for NMR test directly without further purification.

Results and discussion

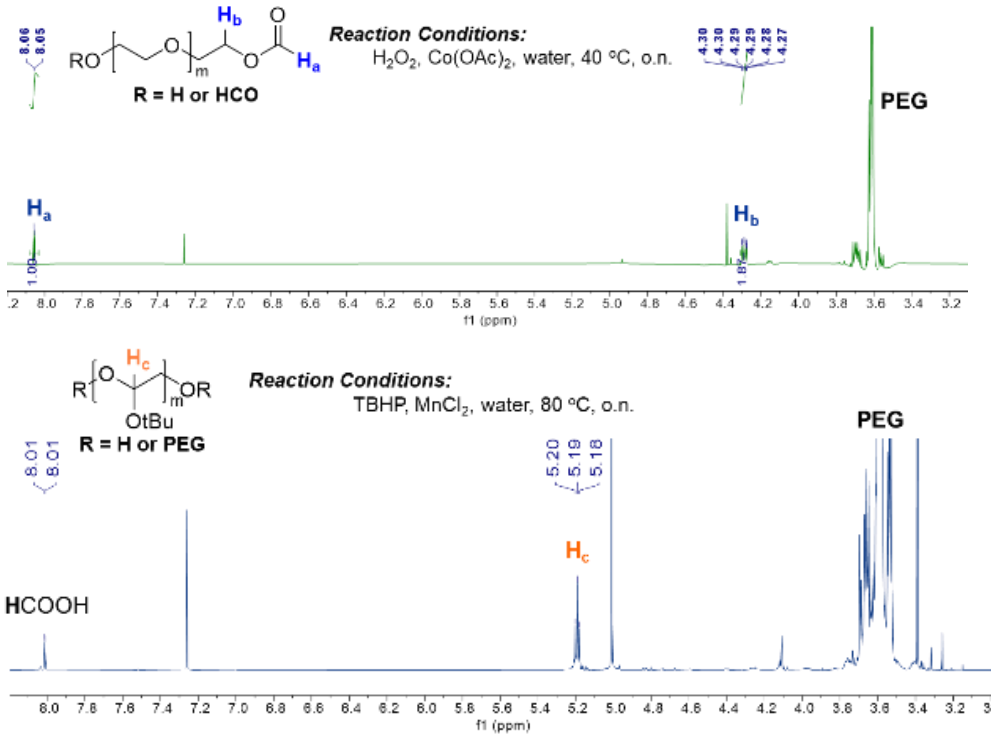
Scheme 1 Transit metal catalyzed oxidative degradation of polyethylene glycol

1. Oxidant and catalysts reagent pairs screening

Cata. \ Oxi.	**TBHP[b]**	**H_2O_2[c]**	**BzO_2[b]**	***m*CPBA[b]**
$FeCl_2$	●	×	●	●
$MnCl_2$	√	×	×	●
$Co(OAc)_2$	√	√	×	×
$CuSO_4$	√	×	×	●
$VOSO_4$	√	●	●	●

a: 100 mg PEG, 0.5 eq. oxidant, 6.0 mg cat., 2.0 mL water, o.n., catalysts are metal salts with hydrate. √ indicates oxidized and hydrolysis products. ● indicates hydrolysis products only; × indicates no reaction. b: 80 °C; c: 40 °C.

2. NMR spectrum for oxidative products

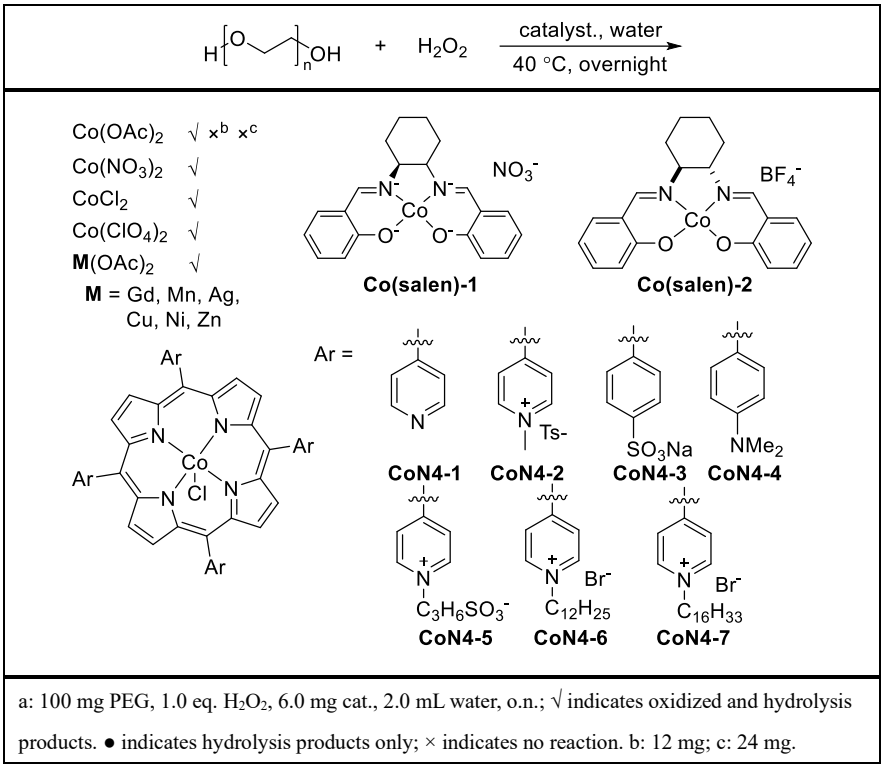


The oxidative degradation of polyethylene glycol (PEG) was explored using various combinations of oxidants and metal catalysts to optimize conditions for effective hydrolysis chain scission with oxidative product formation (Scheme 1.1). Among the tested conditions, cobalt acetate with H_2O_2 at 40 °C gave the oxidized and hydrolyzed PEG products (Scheme 1.2.a). TBHP was also effective with $MnCl_2$, $Co(OAc)_2$, $CuSO_4$, and $VOSO_4$ at 80 °C, producing a different series of products (Scheme 1.2.b). While benzoyl peroxide and *m*CPBA showed less efficiency. These preliminary results indicated the importance of matching oxidant with metal catalysts properly. Significantly, TBHP could only give a tert-butoxide adducted product, and H_2O_2 provided a formate ester type product, which could be generated from beta-scission between C-C bonds in ethylene glycol unit. Thus, we chose cobalt acetate and hydrogen peroxide as the degradation reagents pair for the further studies.

A series of screening were then performed to better understand how the catalyst structure affects reaction efficiency. As a simple and readily available cobalt catalyst, cobalt acetate exhibits good oxidation and hydrolysis activity in aqueous solution, and its performance is higher than that of other catalysts The usage of cobalt nitrate and some other heme-cobalt complex (**CoN4-1,3,4**) also gave the desired product. Interestingly, by

using **Co(salen)-1** and **Co(salen)-2**, with the same ligand, the reaction showed different activity, which indicates the importance of anions of catalyst. Moreover, all other metal acetate salts would not provide oxidation reaction efficiently.

Table 1 Catalysts screening for oxidative degradation of PEG[a]



a: 100 mg PEG, 1.0 eq. H_2O_2, 6.0 mg cat., 2.0 mL water, o.n.; √ indicates oxidized and hydrolysis products. ● indicates hydrolysis products only; × indicates no reaction. b: 12 mg; c: 24 mg.

Also, we have tested the oxidative degradation of PEG under different catalyst loadings. Initial experiment without any catalyst resulted solely in the detection of hydrolysis products. The introduction of $Co(OAc)_2$ at 1.7 mol% successfully yielded the desired products. However, increasing the catalyst loading to 8.7 mol% and 17.4 mol% did not enhance the reaction outcome; in fact, no oxidized or hydrolyzed products were observed. This suggests that excessive catalyst concentrations might suppress the reaction, potentially due to the extremely fast decomposition of hydrogen peroxide. These results underscore the importance of optimizing catalyst loading to achieve effective oxidative degradation of PEG, that a finely tuned balance between the generation of active oxidative species and the oxidation of PEG substrates should be stroke to ensuring efficient conversion of PEG to desired products.

We have established a non-biological strategy with cobalt acetate as catalyst and hydrogen peroxide as oxidant for PEG oxidative degradation at 40 °C under aqueous

conditions. While optimisation of the catalyst loading demonstrated that 1.7 mol % could achieved a relatively good performance in efficiency and selectivity. This cobalt-based catalytic system has shown good potential in the oxidative degradation of PEG, providing a supportive indication for the development of sustainable polymer recycling technologies.

(2) Different PEG Chain Lengths and Model Molecule Exploration

Oxidative degradation of PEG

To a 4 mL vial with a rubber cap, was weighed 100 mg PEG with different chain lengths, 6.0 mg $Co(OAc)_2 \cdot 4H_2O$ (2.3 μmol, 1.0 mol %), and 2.0 mL DI water. The mixture was stirred for 0.5 min to form a clear solution, followed by adding 230 μL H_2O_2 (35% w/w, 2.3 mmol, 1.0 equiv.). Then the reaction was stirred for different hours or overnight under 40 °C oil bath. After desired reaction time, the reaction mixture was extracted by chloroform and diluted for NMR test directly without further purification.

Results and discussion

Table 2 Degree of Oxidation for PEG of Different Molecular Weights

entry	substance	DO
1	PEG600	1/9
2	PEG2000	1/9
3	PEG4000	1/12
4	PEG6000	1/13
5	PEG20000	1/63

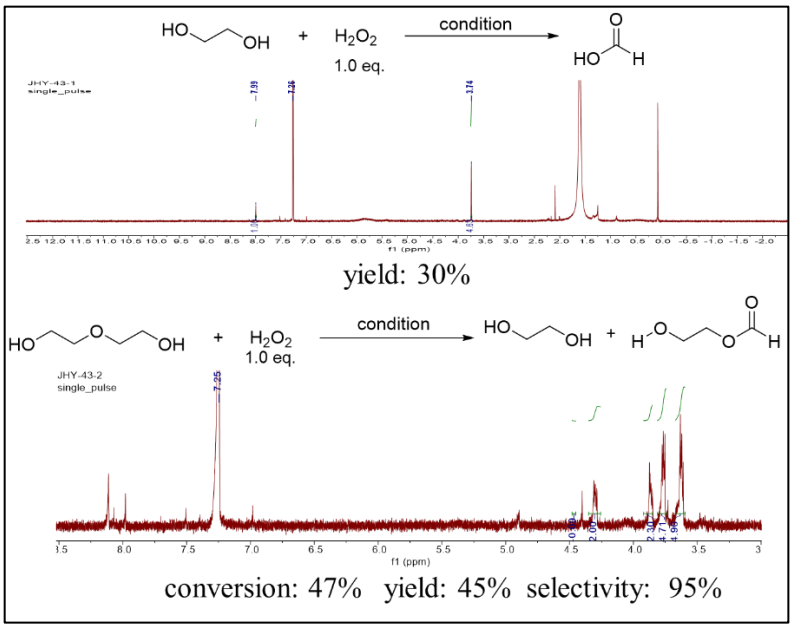
100 mg PEG, 0.5 eq. oxidant, 6.0 mg cat., 2.0 mL water, o.n., catalysts are metal salts with hydrate.

To evaluate the generality and molecular weight dependence of the cobalt acetate/H_2O_2 system, we investigated the oxidative degradation of polyethylene glycol (PEG) with varying chain lengths (Mn = 600 to 20,000 Da) under identical conditions (1.0 equiv. H_2O_2, 1.0 mol% $Co(OAc)_2$, 40 °C, overnight). The degree of oxidation (DO) was determined by quantitative ^1H NMR analysis using terminal formate signals as markers.

As shown in the table, PEG600 and PEG2000 both exhibited a degree of oxidation of 1/9, indicating a similar extent of chain cleavage under these conditions. However, as the molecular weight of PEG increased, a gradual decrease in DO was observed: 1/12 for PEG4000, 1/13 for PEG6000, and only 1/63 for PEG20000. These results suggest that longer PEG chains are less efficiently cleaved under the same oxidative conditions, possibly due to increased steric hindrance, decreased solubility, or reduced diffusion rates in aqueous media.

The data further indicate that while the $Co(OAc)_2/H_2O_2$ system remains catalytically active across a wide molecular weight range, however, the efficiency of oxidative scission is significantly affected by chain length. This highlights the importance of optimizing reaction conditions (e.g., oxidant concentration, temperature, or reaction time) for high-molecular-weight PEGs in future applications.

Table 3 Degree of Oxidation for EG and DEG



100 mg EG, DEG, 0.5 eq. oxidant, 6.0 mg cat., 2.0 mL water, o.n., catalysts are metal salts with hydrate.

To explore the oxidative reaction mechanisms on polyethylene glycol (PEG), this experiment utilized its monomer, ethylene glycol (EG), and dimer, diethylene glycol (DEG), instead of PEG itself. This approach allows for a clearer analysis and understanding of the specific processes involved in oxidation reactions. We employed ^1H NMR spectroscopy to analyze the reaction products to determine their structures and types of reactions.

Analysis of Ethylene Glycol (EG) using NMR: Under the specified reaction conditions, the top NMR spectrum displays the oxidative products of ethylene glycol. As EG is a monomer, it undergoes no hydrolysis, only oxidative reactions. The sharp signal at $\delta = 8.0$ ppm is attributed to the formate proton, indicating the formation of formic acid through oxidative cleavage at the terminal EG unit. The conversion rate and yield of EG are directly related to the formation of formic acid. This result indicates that EG is efficiently converted into formic acid under these conditions.

Analysis of Diethylene Glycol (DEG) using NMR: The bottom spectrum shows diethylene glycol under the same conditions. Since DEG includes two ethylene glycol units, it could undergo both oxidation and hydrolysis reactions. The NMR spectrum displays signals at $\delta = 8.0$ ppm for the formate proton and $\delta = 4.2$ ppm for the ethylene glycol proton.

The analysis of conversion rates and yields below the spectra indicates that the formation of the primary cleavage products significantly contributes to the overall conversion rate. From the integral ratios of H_a and H_b signals to the backbone signals, we determined that the conversion rate for DEG is approximately 47%with the 45% yield of formate ethylene glycol ester, that approximately 95% of the reacted DEG converted to formate-terminated fragments, indicating high selectivity of the oxidation process towards the formation of monoesters.

Together, these results confirm that the cobalt acetate/H_2O_2 system effectively induces oxidative cleavage of PEG under mild aqueous conditions, producing formate and formate ester-terminated fragments as the primary products. The NMR analysis provides direct structural evidence of PEG oxidation and validates the degree of oxidation calculations based on the integral ratios of Ha, Hb, and backbone signals. These findings further support the system's applicability to a wide range of PEG materials, highlighting the need for further optimization of reaction conditions to enhance the degradation efficiency of ultra-high-molecular-weight PEGs.

This study successfully demonstrated the oxidative cleavage mechanisms of ethylene glycol (EG) and diethylene glycol (DEG) using a cobalt acetate/H_2O_2 system under mild aqueous conditions. The use of 1H NMR spectroscopy provided clear, structural

insights into the oxidative products, confirming efficient conversion of EG to formic acid and highlighting the more complex oxidative and potential hydrolytic reactions occurring in DEG. Notably, the system exhibited high selectivity for forming monoesters, particularly formate-terminated fragments, with a significant conversion rate observed for both substrates. The results affirm the potential of this oxidative system to process a range of polyethylene glycol materials, emphasizing the importance of optimizing reaction conditions to enhance the degradation efficiency, especially for high-molecular-weight PEGs. This study lays a robust foundation for further exploration and application of oxidative degradation strategies in polymer recycling and degradation.

(3) Hydrogen Peroxide Addition Method and Amount

Oxidative degradation of PEG

Weigh 100 mg of PEG-2000 (2.3 mmol of repeating units) into a 4 mL vial with a rubber cap. Add 6.0 mg of cobalt(II) acetate tetrahydrate ($Co(OAc)_2 \cdot 4H_2O$) (2.3 μmol, 1.0 mol%) and 2.0 mL of deionized water. Stir the mixture for 0.5 minutes until a clear solution forms. Then 230 μL of hydrogen peroxide (35% w/w, 2.3 mmol, 1.0 equiv.) was diluted to 0.90 mL or 0.45 mL by water and added dropwise via a syringe pump. The reaction was stirred for 22 hours in a 40°C oil bath. After the desired reaction time, the reaction mixture was extracted with chloroform and diluted directly for NMR testing without further purification.

Results and discussion

Table 4 Different H_2O_2 Addition Rate on Oxidative Degradation

entry	cat.	flow rate	DO
1	$Co(OAc)_2$	0.9 ml/2 h	1/15
2		0.9 ml/5 h	1/22
3		0.45 ml/5 h	1/7.5

100 mg PEG, 6.0 mg catalyst, 2.0 mL water. H_2O_2 is added by syringe pump.

Catalysts used are metal salts with hydrate form.

This study further investigated the effects of hydrogen peroxide (H_2O_2) addition rate and dosage on the oxidative degradation of polyethylene glycol (PEG). Four controlled dropwise addition experiments were conducted (0.9 mL over 5 hours, 0.9 mL over 2 hours, and 0.45 mL over 5 hours) to evaluate how the gradual release of the oxidant influences the reaction process. The results indicated that slow addition helps regulate the generation rate of reactive oxidative species, meanwhile the initial concentration of H_2O_2 performs an extremely important part in improving the oxidation degree. However, a further research is required to investigate the relevance among those factors.

Table 5 Different Initial H_2O_2 Dosage on Reaction

entry	Oxidant	eq.	DO
1	H2O2	100%	1/12
2		200%	1/12
3		300%	1/9
4		400%	1/7
5		500%	1/7

100 mg PEG, 6.0 mg catalyst, 2.0 mL water. Catalysts used are metal salts with hydrate form.

In addition, a series of experiments were performed in which different equivalents of H_2O_2 (1–5 equiv.) were added all at once at the beginning of the reaction. It was observed that moderate dosages (e.g., 1.0–2.0 equiv.) facilitated the formation of both oxidative and hydrolytic products. In contrast, excessive amounts of H_2O_2 (entry 5) appeared to suppress the reaction, likely due to rapid peroxide decomposition, leading to reduced yield or complete reaction inhibition.

This study has determined the optimal conditions for the oxidative degradation of polyethylene glycol (PEG) using cobalt acetate and hydrogen peroxide. Experiments demonstrated that controlling the slow addition of hydrogen peroxide effectively regulates the reaction, optimizes product selectivity, and reduces side reactions. These findings provide important technical support for developing efficient polymer recycling technologies and highlight the significance of precisely controlling the rate and dosage of hydrogen peroxide addition.

(4) Additive Screening

Oxidative degradation of PEG

To a 4 mL vial with a rubber cap, was weighed 100 mg PEG-2000 (2.3 mmol to repeating units), 6.0 mg $Co(OAc)_2 \cdot 4H_2O$ (2.3 μmol, 1.0 mol %), additives were added simultaneously, and 2.0 mL DI water. The mixture was stirred for 0.5 min to form a clear solution, followed by adding 230 μL H_2O_2 (35% w/w, 2.3 mmol, 1.0 equiv.) via syringe. Then the reaction was stirred for 22 hours under 40 °C oil bath. After desired reaction time, the reaction mixture was extracted by chloroform and diluted for NMR test directly without further purification.

Results and discussion

Table 6 The results of adding different additives

entry	additive	result
1	MSA	n.r.
2	TfOH	n.r.
3	HNO_3	n.r.
4	HCl	n.r.
5	HCOOH	√
6	AcOH	n.r.
7	$Ti(OiPr)_4$	n.r.

entry	additive	eq.cat	DO
1	Na(OAc)	10%	n.r.
2		20%	n.r.
3		30%	n.r.
4	$Co(NO_3)_2$	10%	1/20
5		20%	1/30
6		30%	1/26
7		40%	1/31

a: 100 mg PEG, 0.5 eq. oxidant, 6.0 mg cat., 2.0 mL water, o.n., catalysts are metal salts with hydrate.

√ indicates oxidized and hydrolysis products.

Results and discussion

This study investigated the effects of various additives on the oxidative degradation of PEG. The experiment included a range of chemical additives to assess their impact on the reaction efficacy, measured as degrees of oxidation (DO). The additives tested include methanesulfonic acid (MSA), trifluoromethanesulfonic acid (TfOH), nitric acid (HNO_3), hydrochloric acid (HCl), formic acid (HCOOH), acetic acid (AcOH), and titanium isopropoxide ($Ti(OiPr)_4$), each in differing concentrations when applicable.

The results indicate that most of the tested additives showed no significant reaction

(n.r.), suggesting they do not facilitate or participate in the oxidative degradation of polyethylene glycol (PEG) under the tested conditions. Notably, only formic acid (HCOOH) showed a positive result (indicated by ●). However, this positive result may be due to the formic acid detected by NMR, which was initially added as an additive.

In a separate set of experiments, different concentrations of sodium acetate (Na(OAc)) and cobalt(II) nitrate ($Co(NO_3)_2$) were tested as equimolar catalysts (eq.cat), with concentrations ranging from 10% to 40%. The results from these trials indicate that increasing the concentration of $Co(NO_3)_2$ leads to a decrease in the degree of oxidation, from 1/20 at a 10% concentration to 1/31 at a 40% concentration. This suggests that higher concentrations of cobalt ions may reduce the formation of reactive oxidative species, thereby inhibiting PEG degradation.

This study investigated the effects of various additives, including methanesulfonic acid and trifluoromethanesulfonic acid, on the oxidative degradation of polyethylene glycol (PEG). The results showed that these additives did not facilitate the enhancement of PEG oxidation. Additionally, it was found that excessively high concentrations of cobalt ions and acetates might inhibit the oxidation process.

4. Conclusion

The comprehensive study presented systematically investigates the oxidative degradation of polyethylene glycol (PEG) using a cobalt acetate and hydrogen peroxide catalytic system under various experimental conditions. Through meticulous experimentation, the research highlights the significant influence of catalyst type, oxidant concentration, PEG molecular weight, and additive presence on the efficiency and selectivity of PEG degradation.

Key findings from this research demonstrate that cobalt acetate, when paired with hydrogen peroxide, provides a robust catalytic system that effectively induces oxidative

cleavage of PEG, forming formate and formate ester-terminated fragments as primary products. The degree of oxidation varies with the molecular weight of PEG, with shorter chains exhibiting higher degradation efficiencies. This suggests a potential limitation in the application of this catalytic system for higher molecular weight PEG, where steric hindrance and solubility issues may impede the oxidation process.

Additionally, the study explores the impact of varying hydrogen peroxide addition rates and initial dosages, concluding that a controlled, slow addition of the oxidant optimizes the reaction by regulating the generation of reactive oxidative species, thus enhancing product selectivity and reducing side reactions. The results affirm that moderate oxidant dosages facilitate the formation of desired oxidative products without suppressing the reaction kinetics through rapid peroxide decomposition.

The investigation into the effects of various additives revealed that most do not significantly influence the oxidation process, except for formic acid, which shows potential involvement in the reaction mechanism. However, increasing concentrations of cobalt ions and other metal acetates were found to inhibit the reaction, possibly due to the excessive formation of inactive species or competitive reactions that detract from the primary oxidative pathway.

Overall, this study lays a solid foundation for the optimization of cobalt acetate and hydrogen peroxide-based systems for efficient polymer recycling technologies. It underscores the necessity of fine-tuning reaction conditions, such as catalyst loading, oxidant dosage, and reaction environment, to maximize the degradation efficiency of PEG, particularly for higher molecular weights. These insights pave the way for future research aimed at enhancing the applicability of oxidative degradation strategies in polymer recycling and sustainable materials management.

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